Thermodynamic potentials, microscopic modeling and the Boltzmann Law

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Paths and Cycles

\[ w_{or} = ? \quad w_{gr} = ? \]
\[ q_{or} = ? \quad q_{gr} = ? \]
\[ \Delta U_{or} = ? \quad \Delta U_{gr} = ? \]
\[ \Delta S_{or} = ? \quad \Delta S_{gr} = ? \]
\[ w_{cyc} = ? \]
\[ q_{cyc} = ? \]
\[ \Delta U_{cyc} = ? \]
\[ \Delta S_{cyc} = ? \]
Paths and Cycles

\[ w_{or} = p_1(V_1 - V_2) \]
\[ q_{or} = ? \]
\[ \Delta U_{or} = C_V \frac{p_2 V_2 - p_1 V_1}{nR} \]
\[ \Delta S_{or} = ? \]

\[ w_{gr} = p_1 V_1 \ln\left(\frac{V_1}{V_2}\right) \]
\[ q_{gr} = p_1 V_1 \ln\left(\frac{V_2}{V_1}\right) \]
\[ \Delta U_{gr} = 0 \]
\[ \Delta S_{gr} = nR \ln\left(\frac{V_2}{V_1}\right) \]

\[ w_{cyc} = ? \]
\[ q_{cyc} = ? \]
\[ \Delta U_{cyc} = ? \]
\[ \Delta S_{cyc} = ? \]
Carnot cycle: p-V diagram

\[
\frac{V_A}{V_B} = \frac{V_D}{V_C}
\]
Carnot cycle: Best way to convert heat to work

\[ \Delta S = nR \ln \left( \frac{V_B}{V_A} \right) \]

\[ \Delta S = nR \ln \left( \frac{V_D}{V_C} \right) \]

Work = heat that ‘stays’:

\[ w = \Delta S (T_h - T_c) \]

1: \( T \equiv T_h = \text{const.} \)
2: \( q = 0 \)
3: \( T \equiv T_c = \text{const.} \)
4: \( q = 0 \)

Efficiency:

\[ \eta = \frac{T_h - T_c}{T_h} \]
Hurricanes as Carnot cycles

- A: Air bubble takes up heat from the ocean
- B: Bubble expands further and rises up in the atmosphere
- C: Bubble releases heat into atmosphere
- D: Bubble shrinks further & sinks down to the ocean surface

Hurricane Irma, 2017
Free energies and Enthalpy

System
Black Box

Constraints

Perturbation

Response
The variables \((S, V, N)\) or \((U, V, N)\) are not easy to control (or measure) experimentally.

Experimentally it is easier to fix \(T\). Then heat exchange is possible, and \(U\) can fluctuate. Or fix \(p\). Then \(V\) can fluctuate. Or fix \(\mu\), then \(N\) can fluctuate.

**How can we change variables?**
Changing variables: from $S$ to $T$

Heat bath: it can maintain $T = \text{constant}$. Preferred independent variables: $(T, V, N)$.

Put a system in a heat bath with $T$, $V$ and $N$ held constant.

\[
dS_{\text{Comb}} = dS_{\text{Syst}} + dS_{\text{Bath}} \geq 0 \quad \text{(MaxEnt)}
\]

\[
dU_{\text{Comb}} = dU_{\text{Syst}} + dU_{\text{Bath}} = 0 \quad \text{(Energy conservation)}
\]

\[
dS_{\text{Bath}} = \frac{dU_{\text{Bath}}}{T} = -\frac{dU_{\text{Syst}}}{T}
\]

\[
dS_{\text{Syst}} - \frac{dU_{\text{Syst}}}{T} \geq 0 \Rightarrow dU_{\text{Syst}} - TdS_{\text{Syst}} \leq 0
\]

A new state function...
The Helmholtz Free Energy, $F$

$$dS_{Comb} = dS_{Syst} + dS_{Bath} \geq 0$$ is equivalent to $$dF_{Syst} = dU_{Syst} - TdS_{Syst} \leq 0$$

MaxEnt for combined system

Free energy minimization for system

$$F = U - TS$$ is the Helmholtz Free Energy.

$$dF = dU - TdS - SdT = dU - TdS$$ for $T=\text{const.}$

$U = \text{min}$  $S = \text{max}$

The system in the test tube will tend both towards high entropy and low energy.
Example: A simple model of dimerization

$N=2$ gas particles are in a “test tube” of $V$ lattice sites. $T$ is held constant. When the particles occupy adjacent sites, they form a bond of energy $-\varepsilon$.

1. Dimer:

\[
W = V - 1
\]

\[
F_{\text{Dimer}} = U - TS \approx -\varepsilon - kT \ln(V)
\]

2. Monomers:

\[
W = \frac{V!}{2!(V-2)!} - (V - 1) = \frac{(V-2)(V-1)}{2} \approx \frac{V^2}{2}
\]

\[
F_{\text{Monomer}} = U - TS \approx -kT \ln(\frac{V^2}{2})
\]

(assume:
they form bonds when adjacent.
subtract when they are adjacent)
Either $S$ or $U$ wins depending on temperature

\[ F_{\text{Dimer}} \approx -\varepsilon - kT \ln(V) \]

Low $T$: dimer form prevails, $F_{\text{dimer}} < F_{\text{monomer}}$

\[ F_{\text{Monomer}} \approx -kT \ln(V^2 / 2) \]

High $T$: monomer form prevails, $F_{\text{dimer}} > F_{\text{monomer}}$

Dissociation temperature $T_0$: dimer and monomer equally stable, $F_{\text{dimer}} = F_{\text{monomer}}$

\[ F_{\text{Dimer}} = F_{\text{Monomer}} \]

\[ \varepsilon = kT_0 \ln(V / 2) \]

\[ T_0 = \frac{\varepsilon}{k \ln(V / 2)} \]
Fundamental equation: Helmholtz Free Energy

Helmholtz Free Energy:

\[ F = F(T, V, N) = U - TS \]

has minimum when e.g., \( T \) is controlled at the boundaries

Differential form:

\[ dF = d(U - TS) = dU - TdS - SdT \]

\[ dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j \]

\[ dF = \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \sum_{j=1}^{M} \left( \frac{\partial F}{\partial N_j} \right)_{T,V,N_{i\neq j}} dN_j \]

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{V,N} \]

\[ p = -\left( \frac{\partial F}{\partial V} \right)_{T,N} \]

\[ \mu_j = \left( \frac{\partial F}{\partial N_j} \right)_{T,V,N_{i\neq j}} \]

Entropy (extensive)

Pressure (intensive)

Chemical potential (intensive)
The Enthalpy, $H$ (controlling the pressure)

Enthalpy is defined as:

$$H = H(S, p, N) = U + pV$$

= energy of particles + energy of ‘making room’ for the system

Differential form:

$$dH = d(U + pV) = dU + pdV + Vdp = \delta q + \delta w + pdV + Vdp$$

$$dH = TdS + Vdp + \sum_{j=1}^{M} \mu_j dN_j$$

= 0 when $S$ is controlled (tends to a minimum)

Rarely used as an extremum principle ($S$ is hard to control).

However, it can be obtained from calorimetry experiments.

At constant pressure:  
$$dH = \delta q$$  
$$C_p = \left( \frac{\delta q}{dT} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

$$\Delta H = \int_{T_1}^{T_2} C_p(T) dT$$
The Gibbs Free Energy (controlling $p$ and $T$)

Gibbs Free Energy – very important, because $p$ and $T$ are easy to control.

$$G = G(T, p, N) = H - TS = F + pV = \text{‘free enthalpy’}$$

Differential form:

$$dG = d(H - TS) = dH - TdS - SdT$$

$$dG = -SdT + Vdp + \sum_{j=1}^{M} \mu_j dN_j = 0 \text{ for } G \text{’s minimum when } T \text{ and } p \text{ are controlled}$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_{p,N} dT + \left( \frac{\partial G}{\partial p} \right)_{T,N} dp + \sum_{j=1}^{M} \left( \frac{\partial F}{\partial N_j} \right)_{T,p,N_{i\neq j}} dN_j$$

$$S = -\left( \frac{\partial G}{\partial T} \right)_{p,N}$$  
Entropy (extensive)

$$V = \left( \frac{\partial G}{\partial p} \right)_{T,N}$$  
Volume (extensive)

$$\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T,p,N_{i\neq j}}$$  
Chemical potential (intensive)
Maxwell’s relations, susceptibilities, and partial molar properties
A recipe for finding Maxwell’s relations

Assume that we want to find how the entropy depends on volume: \( \left( \frac{\partial S}{\partial V} \right)_{T,N} \)

1). Identify the independent variables: \( (V, T, N) \).

2). Find the natural thermodynamic function for these variables: \( F(T, V, N) \).

3). Express the total differential of the natural function:

\[
dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j
\]

4). Based on Euler’s relations, set equal the relevant cross-derivatives:

\[
\left( \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_V \right)_T = \left( \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_V \right)_T \rightarrow \left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial p}{\partial T} \right)_{V,N}
\]

By measuring how pressure depends on temperature:
We learn how entropy depends on volume! ☺
More thermodynamic functions needed!

What is the area of a lipid bilayer at:

\[ T=310 \text{ K} = \text{const.} \]
\[ p=1 \text{ atm} = \text{const.} \]

Lipid bilayers can change their surface area per molecule, \( A \).
The value of \( A \) at equilibrium could be found by minimizing \( G(T, p, N, A) \)... But so far we do not have a \( G(T, p, N, A) \)!
How to generalize thermodynamic potentials?

Introduce new extensive variable(s) $X$ into the fundamental energy equation:

$$U = U(S, V, N, X)$$

Generalized force is defined as:

$$\mathcal{F}_j = \left( \frac{\partial U}{\partial X_j} \right)_{S,V,N,X_{i\neq j}}$$

Each extensive degree of freedom has a conjugate force:

- $p$ is conjugate force for $V$
- $T$ is conjugate force for $S$
- $\mu$ is conjugate force for $N$
- $F$ is conjugate force for $L$
- $\gamma$ is conjugate force for $A$
- $\psi$ is conjugate force for $Q$
- $B$ is conjugate force for $I$

...and so on.

$$dU = TdS - pdV + \sum_j \mu_j dN_j + fdL + \gamma dA + \psi dQ + BdI + \sum_j \mathcal{F}_j dX_j$$
Example: surface area and surface tension

Assume that surface area can change independently of the volume. Start with \( U \) (always). The variables are: \((T, p, N, A)\). Then add a new term.

\[
U = U(S, V, N, A)
\]

\[
dU = TdS - pdV + \sum_j \mu_j dN_j + \gamma dA
\]

\[
\gamma = \left( \frac{\partial U}{\partial A} \right)_{S,V,N}
\]

\((S, V, N, A)\) are difficult to control. \((T, p, N, A)\) would be desired. Switch to \( G \).

\[
G = U + pV - TS
\]

\[
dG = dU + pdV + Vdp - TdS - SdT
\]

\[
dG = -SdT + Vdp + \sum_j \mu_j dN_j + \gamma dA
\]

\[
\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,p,N}
\]

We will have to minimize \( G \) to find the equilibrium.
Surface forces in the Langmuir trough

The surface tension equals surface pressure.

\[ S(A) = k \ln(W) = Nk \ln(A) \]

\[ dG = -SdT + Vdp - \pi dA \]

\[ \left( \frac{dS}{dA} \right)_{T,p} = \left( \frac{d\pi}{dT} \right)_{p,A} = \frac{Nk}{A} \]

(Maxwell relation)

\[ \pi A = NkT \quad \text{Two-dimensional ideal gas law} \]
Retraction of rubber band: Due to energy or entropy?

Start with the fundamental energy equation:

\[ dU = TdS - pdV + fdL \]

If \( T \) and \( p \) are constant, the natural function is:

\[ dG = -U + pV - TS = H - TS \quad \rightarrow \quad dG = -SdT + Vdp + fdL \]

\[
\begin{align*}
    f &= \left( \frac{dG}{dL} \right)_{T,p} = \left( \frac{dH}{dL} \right)_{T,p} - T \left( \frac{dS}{dL} \right)_{T,p} \\
    \left( \frac{dS}{dL} \right)_{T,p} &= -\left( \frac{df}{dT} \right)_{p,L} \\
    \left( \frac{dH}{dL} \right)_{T,p} &= f - T \left( \frac{df}{dT} \right)_{p,L}
\end{align*}
\]

(Maxwell relation: a way to measure)